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16. ABSTRACT

Particles were collected in dichotomous samplers at three sites in the Philadelphia area during summer, 1982, and analyzed by x-ray fluorescence, instrumental neutron activation, pyrolysis, and ion chromatography. An intermethod comparison showed that fine fraction results agreed within measurement error for S, Ca, Mn, Fe, Zn and Sb. A composite of chemical mass balance, multiple linear regression, and stratification by wind direction was used to apportion mass into ten categories. Primary emissions from residual oil combustion, catalytic crackers, an antimony roaster,and municipal incinerators contributed less than 10% of PM-10. The portions of average PM-10 attributed to crustal matter and vehicle exhaust were 17 ± 2 and 6 ± 2, respectively. That attributed to sulfate plus related water and ions was 50 to 55%. Wind stratified data indicated that 80 ± 20% of the sulfate was from a regional background, Multiple linear regression of S vs tracers Se and either V or Ni indicated that 72 ± 8 and 16 ± 5% could be attributed to coal- and residual oil-fired power plants,respectively.

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A Composite Receptor Method Applied to Philadelphia Aerosol

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■ A composite of chemical mass balances, multiple linear regression, and wind trajectory receptor models was developed to apportion particulate mass into source categories. It was applied to 156 aerosol samples collected in dichotomous samplers at three sites in the Philadelphia area and analyzed by X-ray fluorescence, instrumental neutron activation, ion chromatography, and pyrolysis. The largest component accounted for 49–55% of the mass of ≤10 μm diameter particles and consisted of sulfate plus related ions and water. Other components were crustal matter (17–24% of the mass) and vehicle exhaust (4–6% of the mass). Less than 5% of the mass was attributed to primary emissions from five types of stationary sources. Wind-stratified data indicated that 80 ± 20% of the sulfate was from a regional background. Multiple linear regression attributed 72 ± 8 and 16 ± 5% of S to coal- and oil-fired power plants, respectively.

Introduction

Receptor models are used to resolve the composition of atmospheric aerosol into components related to emission sources (*1–3*). When the chemical mass balance (CMB) receptor model is applied to element concentrations measured by X-ray fluorescence (XRF), four to eight components can typically be resolved on the basis of known chemical signatures (*4*). A difficulty is that the required signatures are not accurately known for two major components: sulfate and vehicle exhaust. For the former, there is an uncertain amount of water associated with sulfate in particles. For vehicle exhaust, the Pb abundance is difficult to specify in the U.S. because measurements are sparse, and the Pb content in gasoline has been declining rapidly during recent years. Multiple linear regression (MLR) has been used to determine the Pb abundance when Pb is a unique tracer for vehicle exhaust, but as this report demonstrates, motor vehicles are not the only significant source of Pb.

We explore the feasibility of overcoming such problems by using a composite receptor method (combined use of several receptor models). It was tested with data from a field study designed according to recommendations from the Quail Roost II Conference (*5*) and conducted as part of a larger study to evaluate dispersion models (*6, 7*). Ambient aerosol was collected in the PM-10 size range (particle diameter ≤10 μm) at three sites in the Philadelphia area during summer 1982. Source emissions were collected by a dilution–cooling technique at two oil-fired power plants, a coal-fired power plant, a municipal incinerator, an Sb ore roaster, a fluidized catalytic cracker at a refinery, and a secondary Al smelter (*8*). Surface soil and dust were collected at 30 sites and suspended by an aerosol generator (*9*). Ambient, source, and soil samples were collected by dichotomous samplers and analyzed by XRF, instrumental neutron activation analysis (INAA), ion chromatography (IC), and pyrolysis with the exception that INAA was not applied to the soil samples.

Here we report the ambient aerosol measurements and illustrate the precision and accuracy of concentrations by comparing results of different analytical methods. We present a mass apportionment based on the following steps: (a) Wind-trajectory analysis (*10*) was used to identify sources to include in CMB calculations. (b) A new composite method described below used a preliminary CMB to derive a set of adjusted Pb and S concentrations that were then used in MLR to determine abundances of Pb in vehicle exhaust and S in the sulfate component. (c) Final CMBs, based on results of the composite method, were used to apportion mass into nine components. (d) Wind direction stratification was used to detect the relative influences of local and regional sources. (e) MLR of S vs Se and V was used to estimate the particulate S contributions from coal and oil burning.

Measurements

Aerosol samples were collected nearly continuously at the three sites shown in Figure 1 for 12-h periods during the day (0600–1800 EDT) and the night (1800–0600 EDT) between July 14 and August 13, 1982. Site 28, at the Institute for Medical Research in Camden, NJ, was in an industrial, commercial area within 10 km of several large emission sources (Figure 2) and was within 400–500 m of several major roads. Site 12, at Northeast Airport, was in a residential area of Philadelphia with isolated light in-

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Table I. Comparison of XRF, INAA, and IC Results for 50 Paired Fine-Particle Samples from Camden, NJ (Site 28), between July 14 and August 13, 1982[a]

	XRF, ng/m³		other results, ng/m³			ratio of means	
	mean	δ	method	mean	δ	(XRF/other)	R
S	4060	20	IC	3720	70	1.09 ± 0.09	0.97
S	4200	20	INAA	3860	900	1.09 ± 0.14	0.92
K	101	3	INAA	144	12	0.70 ± 0.10	0.94
Ca	40	5	INAA	49	18	0.81 ± 0.11	0.65
V	19	4	INAA	13	0.6	1.43 ± 0.18	0.86
Mn	6	2.3	INAA	6	0.3	1.09 ± 0.15	0.72
Fe	91	3	INAA	94	10	0.97 ± 0.12	0.89
Zn	82	1.5	INAA	92	5	0.89 ± 0.11	0.997
Se	1.2	0.6	INAA	1.8	0.1	0.67 ± 0.10	0.70
Br	29	0.8	INAA	23	0.3	1.27 ± 0.16	0.97
Sb	73	5	INAA	79	4	0.93 ± 0.11	0.998

[a] *R* is the correlation coefficient. δ is the typical amount of random error in individual measurements having concentrations similar to the mean. Uncertainties in the ratios include random error shown above and systematic error discussed in the text.

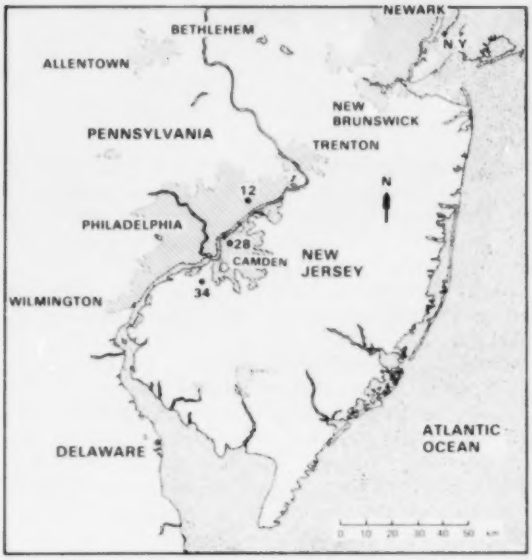

Figure 1. Map showing locations of sampling sites 12, 28, and 32. The diagonally shaded regions indicate urban areas, not political boundaries.

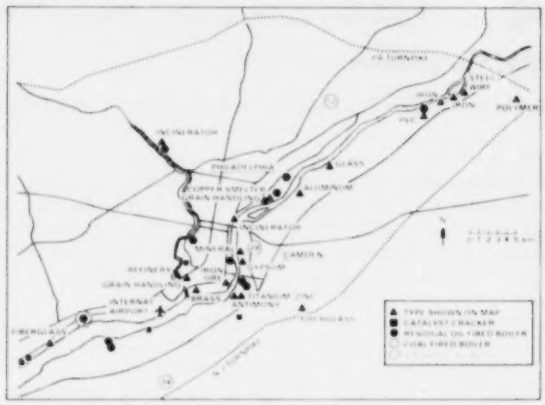

Figure 2. Map showing sampling site locations and point sources having particle emission rates above 50 Mg/y.

dustrial parks; the closest major road was 500 m to the south. Site 34, at Shady Lane Rest Home near Clarksboro, NJ, was in a rural area 1 km northwest of the New Jersey Turnpike. Emission sources in the area are described by Core et al. (*11*).

Automated dichotomous samplers (Beckman Instruments) were used to collect fine (<2.5 μm aerodynamic diameter) and coarse (2.5–10 μm) particles on 2 μm pore size Teflon filters at all three sites. Dichotomous samplers were also used to collect particles on quartz filters (Type 2500 QAST quartz, Palflex Corp.) at sites 12 and 28. Efficiencies for 0.035–1-μm particles were >99.9% for Teflon and ≥91% for quartz (*12*). To improve adhesion, the Teflon filters used to collect coarse particles were coated with 25 μg/cm² of mineral oil before determining tare masses (*13*). The inlets were prototypes of a PM-10 inlet now available from Sierra-Andersen, Inc. Flow rates, set at 1 m³/h, were measured every 5 d in a dry-gas test meter and were constant within 4%. At the end of the study, flow rates were checked by an auditor; deviations ranged from 0 to 12%, and the average was 5%.

Teflon filters were analyzed for mass by β-ray attenuation (*14*, *15*) in a RH = 50% laboratory atmosphere and for elemental composition by an energy-dispersive XRF spectrometer having Ti, Mo, and Sm secondary targets (*16*, *17*). Fine-fraction filters were sent to the University of Maryland for analysis by INAA at the National Bureau of Standards' heavy water reactor (*8*). Pyrolysis of 0.35-cm² portions of quartz filters was used to determine volatilizable carbon (V-C) (650 °C in a He atmosphere) and nonvolatilizable carbon (NV-C) (850 °C in a 98% He, 2% O_2 atmosphere) (*18*). The remainder of each quartz filter was analyzed for sulfate and nitrate by IC and for ammonium by colorimetry (*16*).

Results and Discussion

Precision and Accuracy. Systematic errors were ±7% for sulfate by IC, ±11% for Al by XRF, and ±7% for other elements by XRF. Errors for INAA were the larger of either ±10% or random error determined from counting statistics. Table I lists typical values of random error δ. Table I also shows correlation coefficients and a comparison of mean values for species with mean concentration above δ. For such species, the paired data are highly correlated. The ratios of means agree within overall errors for S, Mn, Fe, Zn, and Sb. For each species measured at site 28, Table II lists average concentration, average uncertainty, and the number of samples having concentration above twice the uncertainty. Variability in the blanks caused the uncertainty for V-C to be large. The data in Tables I and II are based on the 50 sampling periods at site 28 for which we had complete data from all measuring methods.

Ionic Composition. Table I shows that the mean XRF and IC data for fine-particle S agree within measurement

Table II. Aerosol Composition at Site 28 in Camden, NJ, during Summer 1982[a-c]

		fine fraction		coarse fraction	
	method	*N*	av	*N*	av
mass	β-gauge	49	28 700 (3100)	43	11 400 (2800)
NO_3^-	IC	3	130 (160)	37	570 (170)
SO_4^{2-}	IC	50	11 200 (860)	23	520 (300)
NH_4^+	color.	49	3 600 (270)	0	−270 (90)
V-C	pyrol.	25	2 050 (1010)	1	620 (1000)
NV-C	pyrol.	50	1 870 (140)	40	420 (60)
Na	INAA	50	146 (15)		
Al	*d*	50	53 (6)	49	550 (170)
Si	XRF	50	103 (21)	50	1 610 (390)
S	XRF	50	4 200 (290)	50	230 (140)
Cl	XRF	3	3 (5)	41	69 (13)
K	XRF	49	101 (8)	50	151 (23)
Ca	XRF	50	40 (5)	50	360 (40)
Sc*	INAA	50	14 (2)		
Ti	XRF	19	15 (9)	36	65 (12)
V	*d*	50	13 (1.4)	25	7 (4)
Cr	*d*	49	1.5 (0.2)	13	3 (3)
Mn	*d*	50	6 (0.7)	44	11 (3)
Fe	XRF	50	91 (7)	50	490 (40)
Co*	INAA	50	480 (60)		
Ni	XRF	46	11 (1.5)	33	4 (1)
Zn	XRF	50	82 (6)	47	30 (4)
Ga*	INAA	16	76 (84)		
As*	INAA	49	630 (220)		
Se	*d*	50	1.8 (0.2)	2	0.0 (0.5)
Br	XRF	50	29 (2)	50	15 (1.4)
Sr	XRF	10	0.4 (0.6)	39	2 (0.6)
Mo*	INAA	38	880 (360)		
Ag*	INAA	18	167 (120)		
Cd	*d*	24	2.2 (0.7)	1	0 (2)
In*	INAA	12	7 (4)		
Sn	XRF	9	5 (4)	3	1 (3)
Sb	*d*	50	79 (8)	28	181 (13)
I*	INAA	46	1 040 (320)		
Cs*	INAA	23	23 (14)		
La*	INAA	50	1 120 (130)		
Ce*	INAA	45	610 (100)		
Sm*	INAA	50	40 (5)		
W*	INAA	34	230 (60)		
Au*	INAA	27	1.7 (0.9)		
Pb	XRF	50	249 (15)	50	54 (5)

[a] For 50 samples, *N* is the number having concentrations above 2 σ. Data in parentheses represent mean uncertainties. [b] An asterisk (*) denotes data in pg/m³; all other data are in ng/m³. [c] V-C and NV-C pertain to volatilizable and nonvolatilizable carbon, respectively. [d] The method was INAA for fine and XRF for coarse.

error. Because IC detected only sulfate, we conclude that within measurement error, all S occurred as sulfate in the fine fraction. Ammonium and sulfate were highly correlated ($R = 0.97$). The NH_4^+/SO_4^{2-} molar ratios were 1.51 ± 0.11 and 1.72 ± 0.12 for sites 12 and 28, respectively. Data in Table II indicate that any Na, K, Ca, Fe, and Pb cations would contribute <8% of the anion to sulfate molar ratio. We assume that the remaining amount of anion was balanced by H^+ and deduce a H^+/SO_4^{2-} molar ratio of 0.4 ± 0.2. Such a value is a lower limit for H^+ because we did not protect samples from neutralization by NH_3 during 1–14 d of storage in dichotomous samplers.

Table II indicates a significant negative bias for coarse-particle ammonium, which we explain as follows: the dichotomous sampler deposits 10% of the fine particles on the coarse-fraction filter where $(NH_4)_2SO_4$ in fine particles may contact alkaline coarse particles, causing the former to decompose and lose NH_3. When computing species concentrations, we made a mathematical correction for fine particles deposited on the coarse-fraction filter (*16*), assuming zero loss; thus, any loss would cause negative bias.

Nitrate data reported here pertain to nonvolatilized nitrate. Ammonium nitrate is unstable, and the more stable alkaline nitrate compounds may decompose upon contact with acidic fine particles after collection on a filter. Thus, little nitrate was detected in the fine fraction. Most nitrate was collected in the coarse fraction where Ca, a substance often in alkaline form, is abundant and can react with gaseous HNO_3 to form stable $Ca(NO_3)_2$. Little nitrate was detected in source (*8*) or soil (*9*) samples, which suggests that coarse-particle nitrate was produced by reactions in the atmosphere.

Wind-Trajectory Method To Identify Sources To Include in CMB. Following Rheingrover and Gordon (*10*), we used hourly data on surface winds at Philadelphia International Airport to compute resultant wind direction θ and standard deviation δθ for each 12-h period. Also, the mean concentration $\bar{x}$ and standard deviation s were calculated for each species. The wind-trajectory method selected events having $\delta\theta \leq 20°$ and $x \geq \bar{x} + 2s$. The wind direction criterion was satisfied for about 18 of the 12-h periods, and both criteria were satisfied for one or two periods, depending on the species. For periods satisfying both criteria, emission sources were identified when element abundance ratios matched those in source signatures (*8*, *19*).

The wind-trajectory method selected two consecutive periods on July 21–22 with $\theta = 318°$. Then Na, K, Zn, Cd, Sn, and Pb in fine particles at site 28 were at maxima, and element abundance ratios matched within 2σ those measured at the incinerator 15 km northwest of site 28 (*8*). (Here σ includes uncertainty in both source and ambient data.) Another incinerator 4 km northwest of site 28 (Figure 2) could have been a major contributor. Nitrate and Cl also had maxima during the event, but ambient Cl was very deficient and NO_3^- was enriched relative to incinerator emissions (*8*). We attribute the Cl loss and NO_3^- gain to reactions of NaCl and KCl in incinerator particles with atmospheric HNO_3 vapor and H_2SO_4 particles. Similar Cl loss was observed in St. Louis (*10*) and Washington, DC (*20*).

The wind-trajectory method selected other events with elevated Ti and Sb concentrations and indicated a paint pigment plant and an Sb roaster, both 6 km south-southwest of site 28 (Figure 2). On the night of July 18–19, $\theta = 237°$ and Sb concentrations reached maxima of 1.1 and 2.7 μg/m³ for the fine and coarse fractions, respectively. Also selected were events with elevated V, Ni, and Mo concentrations in ratios within 2σ of emissions from oil burning. Other events had elevated La, Ce, and Sm concentrations with ratios that matched catalytic cracker emissions (*8*) within a factor of 2. Several such sources were in the area, but specific ones were not identified. Catalytic cracker emissions were detected only in fine particles because the INAA method, needed to detect tracer elements La, Ce, and Sm, was not applied to ambient coarse particles. However, emissions measured at a catalytic cracker had no significant coarse fraction (*8*).

Time–series plots of coarse particle Cl in Figure 3 show maxima at three sites between August 6 and August 8 (Julian days 218–220). During December 1980, Shaw et al. (*21*) detected the simultaneous occurrence of high Cl concentrations in fine particles in several midwestern states and attributed the event to an intrusion of marine air from the Pacific Ocean. We attribute the event in Philadelphia to marine aerosol from the Atlantic Ocean because the elevated Cl concentrations were mainly in the coarse fraction and because the surface winds on August 6 in Philadelphia, Wilmington, Atlantic City, and Newark were

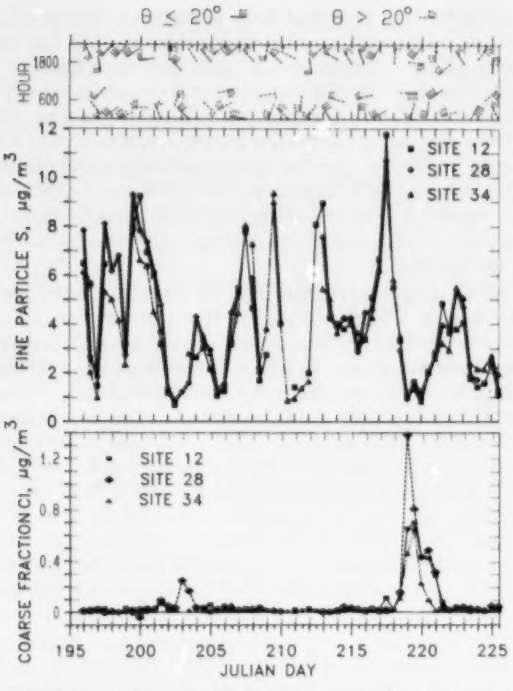

Figure 3. Coarse-particle Cl, fine-fraction S, and 12-h wind resultants between July 14 and August 13, 1982. One, two, three, and four barbs on the wind vectors indicate speeds of 0–5, 5.1–10, 10.1–15, and >15 km/h, respectively. Darts point in direction of airflow.

easterly. Thus, we included a marine component in our coarse-particle CMB.

Composite of CMB and MLR. In a study in Denver during the winter, Lewis et al. (*22*) used MLR to determine abundances of elements in vehicle exhaust, wood smoke, sulfate, and crustal matter. Because atmospheric K, their tracer for wood smoke, included a contribution from soil, they used the measured K concentration minus a correction for soil as a wood-smoke tracer. We could not use the algebraic method of Lewis et al. to derive a Pb tracer for vehicle exhaust because there were multiple sources of Pb, which themselves lacked unique tracers. Rather, we used CMB to determine nonvehicular Pb, which we subtracted from the measured Pb concentration to yield a tracer for vehicle exhaust. Our composite of CMB and MLR is outlined below.

The CMB method expresses the concentration C_i of species i as

$$C_i = \sum_j A_{ij} M_j \quad (1)$$

where A_{ij} is the abundance of species i in component j and M_j is the total mass concentration for component j. Using data on C_i and A_{ij}, unknown values M_j are found by a least-squares method that minimizes the expression

$$\chi^2 = \sum (C_i - O_i)^2 / E_i^2 \quad (2)$$

where O_i is the observed concentration of species i, and E_i^2 is the *effective variance*, which includes the uncertainties in O_i and A_{ij} (*23*).

Two criteria must be met for each species i in eq 2: (a) its abundance in each component must be known, and (b) all its major sources j must be included in eq 1. For our data these criteria could be met for a fine-particle CMB based on Al, Si, Ca, Ti, V, Ni, Zn, Cd, Sn, Sb, La, Ce, and Sm in the following six components: municipal incinerators (*8*), catalytic crackers (*8*), oil combustion by electric utilities (*8*), an Sb roaster (*8*), paint pigment manufacturing (*24*), and local dust (*9*). Using these 13 elements and 6 source signatures, we applied the CMB model to fine-particle data for each 12-h period at all sites to obtain 156 sets of M_i. Then, we calculated

$$O_i' = O_i - \sum A_{ij} M_j \quad (3)$$

where O_i' represents M', [S′], and [Pb′], which are the portions of observed mass, S, and Pb concentrations due only to the vehicle exhaust and sulfate components. We applied a statistical package for MLR (*25*) to all 156 fine-fraction observations and obtained

$$M' = 3546 \pm 774 \text{ ng/m}^3 + (4.91 \pm 0.13)[\text{S}'] + (14.5 \pm 3.2)[\text{Pb}'] \quad (4)$$

and the multiple correlation was $R = 0.95$.

We interpret the reciprocal of the regression coefficient of [S′] in eq 4 as the abundance of S in the regional sulfate component, 20.4 ± 1.4%. The uncertainty includes the standard error in eq 4 and the systematic measurement error for S. Such an abundance is lower than the values 24.2 and 26.1% for S in pure $(NH_4)_2SO_4$ and NH_4HSO_4, respectively. Sulfur abundances ranging from 12 to 20% were obtained by other investigators, who applied MLR and multivariate methods to aerosol data (*22*, *24*, *26*). Water and possibly organic matter retained on acidic sulfate particles during laboratory mass analysis may account for S abundances lower than 24.2%.

Likewise, eq 4 indicates a 6.9 ± 1.6% abundance of Pb in vehicle exhaust. This falls within the range of results obtained by other investigators: 7.0% for a Pennsylvania Turnpike tunnel during 1977 (*27*), 7.2 ± 0.2% for Watertown, MA, during 1979–1981 (*26*), 7.3% for Detroit during July 1981 (*28*), and 4.4 ± 0.6% for Denver during winter 1982 (*22*). The intercept in eq 4, which is comparable to the uncertainty of each mass measurement, may result from mass measurement error or may represent sources not included in the CMB.

Mass Apportionment. Fine-particle mass was apportioned by CMB into eight components and shown in Table III. Vehicle exhaust and sulfate were included with the six components used in the preliminary CMB. For vehicle exhaust, the Pb abundance of 6.9 ± 1.6% was derived from eq 4. Abundances of other elements in vehicle exhaust (S, Cr, Mn, Fe, Ni, and Br) were taken from Pennsylvania Turnpike tunnel data (*27*) adjusted for the vehicle mix in Philadelphia (94% gasoline, 6% diesel from ref 11). The sulfate component included the 20.4 ± 1.4% S abundance derived from eq 4. Concentrations of other elements were from the regional sulfate signature of ref 29 normalized to our S value. The uncertainties in the derived mass components were obtained when χ^2 was minimized (*23*).

Except for Cl, Cr, Se, and I, the measured and calculated element concentrations agree within $\pm 2E_i$, where E_i^2 is the effective variance defined above. Calculated Cl and Br values are too large because our model does not account for volatilization. The regional sulfate component represents most of the calculated Se, but that signature, derived with principal components analysis (*26*, *30*) from Shenandoah Valley data (*29*), does not exactly represent Se in Philadelphia. Most of the measured I is not explained. Deviations for such elements have little effect on our mass apportionment.

We applied CMB as in Table III to each sample; averages for each site are shown in Table IV. The indicated standard errors were obtained by compounding individual error estimates, assuming that they were independent.

Table III. CMB Results for Average Fine-Particle Composition at Camden, NJ (Site 28), between July 14 and August 13, 1982[a,b]

	calcd	measd	crustal	oil	paint pig.	cat. crack.	munic incin	veh exh	Sb roast.	S
V-C	1008 ± 1121	2046	76	16	0	1	4	911	1	0
NV-C	1122 ± 568	1867	11	29	0	0	25	1057	0	0
Na	103 ± 36	146	21	21	0	1	45	16	0	0
Al[c]	39 ± 12	53	16	5	2	14	2	0	0	0
Si[c]	136 ± 37	103	63	17	0	45	12	0	0	0
S[c]	4196 ± 403	4196	1	89	0	28	21	46	1	4010
Cl	223 ± 33	3	0	0	0	0	194	29	0	0
K	64 ± 19	101	6	1	2	0	55	0	0	0
Ca[c]	35 ± 9	40	9	20	4	0	2	0	0	0
Ti[c]	18 ± 9	15	3	1	14	1	0	0	0	0
V[c]	11 ± 3	13	0	11	0	0	0	0	0	0
Cr	1 ± 0	2	0	0	0	0	0	0	0	0
Mn	5 ± 1	6	1	0	0	0	0	2	0	2
Fe	76 ± 22	91	45	11	10	0	2	7	0	0
Co*	706 ± 147	483	17	684	0	3	2	0	0	0
Ni[c]	13 ± 3	11	0	13	0	0	0	0	0	0
Zn[c]	82 ± 8	82	0	7	0	0	71	3	0	1
As*	213 ± 219	632	4	31	0	0	47	0	0	132
Se*	887 ± 233	1800	0	15	0	2	29	0	0	841
Br	70 ± 34	29	0	0	1	0	2	68	0	0
Mo*	666 ± 400	900	11	381	0	0	274	0	0	0
Ag*	50 ± 100	200	0	0	0	0	50	0	0	0
Cd[c]	1 ± 1	2	0	0	0	0	1	0	0	0
In*	9 ± 4	7	0	0	0	0	4	0	0	6
Sn[c]	6 ± 4	5	0	0	0	0	5	0	1	0
Sb[c]	79 ± 9	79	0	0	0	0	1	0	77	0
I*	104 ± 304	1000	0	0	0	0	0	104	0	0
Cs*	9 ± 15	23	5	0	0	0	4	0	0	0
La*[,c]	904 ± 192	1120	13	200	0	690	1	0	0	0
Ce*[,c]	746 ± 177	609	34	155	0	557	0	0	0	0
Sm*[,c]	49 ± 13	40	5	8	0	36	0	0	0	0
W*	51 ± 119	200	51	0	0	0	0	0	0	0
Pb[c]	249 ± 45	249	2	10	0	0	42	180	0	14
mass	24853 ± 3421	28282	742	740	62	223	720	2603	105	19658
δmass	2124	3124	357	131	41	43	82	667	12	1978

[a] An asterisk (*) denotes data in pg/m^3; all other data are in ng/m^3. [b] Calculated species uncertainty E_i is square root of effective variance. [c] Elements included in least-squares fit.

Also indicated are estimates of overall uncertainty due to uncertainty in abundances of key elements in source signatures. The component labeled "other" is the intercept in eq 4 and represents bias or components not included in the CMB. Results for the dust signature are labeled "crustal matter" and represent a broad category that includes minerals and coal fly ash.

The coarse fraction results in Table IV are based on CMB with five components: municipal incinerators (*8*), an Sb ore roaster (*8*), surface dust (*9*), sulfate, and marine aerosol. Elements used in the least-squares fit were Al, Si, S, Cl, Ti, Mn, Zn, Cd, Sn, and Pb. Because ammonium was not present in the coarse fraction (Table II), we used the 33% abundance of S in sulfate for the coarse sulfate component. The marine signature was from ref 19; the Cl abundance was 40%, which is lower than that of dried seawater and represents some loss of Cl. A large uncertainty is shown for the marine component because it was determined almost exclusively by Cl, a volatilizable element. Because we did not constrain our CMB solutions to positive values, negative values below the detection limit were sometimes obtained, as coarse-particle results in Table IV indicate.

Estimating Local and Regional Components. Two facts suggest that the sulfate component, which accounts for 50–55% of PM-10, is not of local origin: (a) Paired S data for site 12 vs site 28 and site 28 vs site 34 were highly correlated (R = 0.93). (b) Time-series plots in Figure 3 show that fine-particle S has similar concentrations at all three sites.

Table IV. Average Mass Balance in ng/m^3 for July 14 to August 13, 1982, Deduced by Composite of CMB and MLR Methods

component	site 12	site 28	site 34	overall uncertainty, %
fine fraction				
crustal matter	1240	870 ± 60	690	50
oil fly ash	480	690 ± 20	440	30
Ti-rich paint pigment	29	53 ± 6	7	30
fluidized catalyst cracker	140	195 ± 9	93	30
municipal incinerators	550	700 ± 20	190	30
antimony roaster	5	94 ± 3	2	10
motor vehicle exhaust	2280	2630 ± 120	1470	20
sulfate, cations and water	18600	19400 ± 320	18500	10
other (MLR intercept)	3550	3550 ± 770	3550	
calculated total	27000	28000 ± 850	25000	10
measured total	27000	28300 ± 440	26000	10
coarse fraction				
crustal matter	6500	8700 ± 210	5200	30
marine	150	210 ± 30	105	50
sulfate	450	590 ± 70	720	30
municipal incinerators	100	44 ± 29	−17	30
antimony roaster	15	230 ± 14	8	10
calculated total	7200	9800 ± 230	5900	20
measured total	7900	11400 ± 400	7900	10
PM-10 (fine + coarse)				
calculated total	34000	38000 ± 900	31000	10
measured total	34900	39700 ± 600	33900	10

To estimate contributions from regional sources, we selected cases when wind direction was steady along the 30–210° line of our samplers (Figure 2). Paired samples at sites 12 and 34 were selected on the basis of having at

Table V. Ratios of Mean Concentrations at Sites 12 and 34 during Steady Winds from SSW and NNE between July 14 and August 13, 1982[a]

species	wind from SSW, site 34/site 12 (N = 11)	wind from NNE, site 12/site 34 (N = 5)
regional		
I-F	1.22 ± 0.32	0.78 ± 0.15
Se-F	0.85 ± 0.17	0.86 ± 0.19
S-F	0.82 ± 0.22	0.78 ± 0.13
mixed		
Ce-F	0.73 ± 0.25	0.40 ± 0.11
Na-F	0.71 ± 0.18	0.51 ± 0.16
Al-F	0.70 ± 0.25	0.80 ± 0.22
Si-F	0.61 ± 0.26	0.94 ± 0.24
K-F	0.60 ± 0.21	0.69 ± 0.22
V-F	0.58 ± 0.13	0.47 ± 0.10
Si-C	0.54 ± 0.17	0.65 ± 0.23
As-F	0.52 ± 0.18	0.92 ± 0.44
Fe-F	0.47 ± 0.17	0.76 ± 0.17
Al-C	0.45 ± 0.16	0.89 ± 0.25
Br-F	0.45 ± 0.06	0.92 ± 0.28
Fe-C	0.38 ± 0.13	0.62 ± 0.18
Pb-F	0.38 ± 0.06	0.74 ± 0.23
Ca-F	0.35 ± 0.15	0.84 ± 0.19
Cr-F	0.33 ± 0.09	0.89 ± 0.17
Ca-C	0.29 ± 0.13	0.67 ± 0.23
Br-C	0.27 ± 0.05	0.66 ± 0.23
Pb-C	0.26 ± 0.05	0.61 ± 0.23
La-F	0.25 ± 0.08	0.13 ± 0.05
Mo-F	0.25 ± 0.12	0.68 ± 0.20
Mn-F	0.23 ± 0.06	0.62 ± 0.15
local		
Ni-F	0.20 ± 0.07	0.45 ± 0.12
Ni-C	0.16 ± 0.09	0.06 ± 0.09
Co-F	0.14 ± 0.05	0.40 ± 0.12
Zn-F	0.11 ± 0.04	1.40 ± 0.50
Zn-C	0.03 ± 0.02	0.72 ± 0.12
Sb-F	0.04 ± 0.04	0.07 ± 0.03
Sb-C	0.00 ± 0.03	0.06 ± 0.14

[a] The classification pertains only to winds from SSW as discussed in the text. F denotes fine and C denotes coarse.

least 75% of the hourly surface wind directions recorded at Philadelphia International Airport in the SSW or NNE quadrant. Table V shows ratios of mean species concentrations for steady wind from NNE (345–75°) and SSW (165–255°) quadrants. The data are sorted according to decreasing values of the ratio site 34/site 12 for winds from SSW, and the sources are labeled "local", "mixed", and "regional" according to the ranges 0–0.2, 0.2–0.8, and 0.8–1. The rationale for this classification is that site 34 is moderately free of upwind urban areas during winds from SSW (see Figure 1). Thus, a ratio $\simeq$0 implies local sources, and a ratio $\simeq$1 implies regional sources. The classification in Table V does not apply to winds from NNE because Figure 1 shows large urban areas NNE of site 12. Emissions from the nearby New Jersey Turnpike SSW of site 34 cause Pb and Br to be classified as mixed.

Table V shows that local sources contribute 95 ± 5% of the Sb, whereas regional sources contribute 80 ± 18% of the S and 85 ± 18% of the Se. Altshuller (*31*) deduced local and regional components for sulfate measured at 45 stations in eastern U.S. between 1963 and 1978. Early in that period, local sources contributed $\simeq$45% of total sulfate during summer months. By 1978 the local component had decreased to $\simeq$25% due to controls on S emissions applied mainly in urban areas (*31*). The regional nature of particulate S in Philadelphia is further indicated in Table II by the average S concentrations being within 20% of summertime values at Great Smoky Mountains National Park (*32*), Shenandoah Valley (*32*), Ohio River Valley (*33*), Newark, NJ (*34*), Detroit (*28*), and St. Louis, MO (*35*), between 1976 and 1981.

Table VI. Apportionment of Sulfur in Fine Particles by MLR and Total Sulfur Dioxide Emission Rates by Category for Various States

method	sulfur from each source, % other	coal	oil	SO_2 emissions,[a] Gg/y
fine-particle MLR				
S vs Se and V	10 ± 9	73 ± 8	17 ± 5	
S vs Se and Ni	14 ± 9	71 ± 8	15 ± 4	
SO_2 emissions from				
Ohio	4	95	1	2813
Indiana	3	93	4	2076
Pennsylvania	10	85	5	2011
West Virginia	4	95	1	1205
Kentucky	5	95	0	1184
New York	10	40	50	934
North Carolina	10	80	10	583
Maryland	13	71	16	359
New Jersey	34	27	39	329
Virginia	16	53	31	313
Delaware	8	42	50	101

[a] Data on SO_2 emission rates during 1980 are from ref 36.

Sources of Particulate Sulfur. An emission inventory summarized in Table VI shows that about 90% of the SO_2, the precursor for particulate S, is emitted from coal- and oil-fired power plants (*36*). Investigators have attributed the S and Se at Shenandoah Valley, VA, to coal-fired power plants (*29*, *32*). In coastal states, power plants burning oil are major sources of S (*36*), V, and Ni.

Assuming that Se and either V or Ni are tracers for coal- and oil-fired power plants, respectively, we used MLR to express fine-particle S as

$$[S] = 380 \pm 355\ ng/m^3 + (1791 \pm 201)[Se] + (67 \pm 21)[V] \quad (5)$$

$$[S] = 555 \pm 342\ ng/m^3 + (1740 \pm 204)[Se] + (74 \pm 22)[Ni] \quad (6)$$

Residuals were approximately normally distributed, and multiple correlations were R = 0.67 for 156 samples. Because S is emitted mainly as SO_2, atmospheric reactions are required to produce particulate S. Therefore, the regression coefficients in eq 5 and 6 represent averages of time-dependent quantities. Variability in the fraction of SO_2 converted to SO_4^{2-} could account for correlations that are only moderately high.

Table VI shows apportionments of S on the basis of the mean of each term in eq 5 and 6 divided by the mean fine-particle S concentration. Table VI also shows amounts of SO_2 emitted by coal- and oil-fired power plants in several states (*36*). The regression results indicate that coal- and oil-fired power plants contribute 72 ± 8% and 16 ± 5%, respectively, to particulate S. Such a result for coal is similar to the 80–95% range of values shown in Table VI for states that are high S emitters south and west of our sampling area.

Summary

A new composite receptor method that combines wind-trajectory analysis, CMB, and MLR was applied to data obtained by XRF and INAA. The combined use of XRF and INAA enabled more sources to be resolved than was possible when only one method was used. The former provided essential data on Si, S, Ni, and Pb; the latter provided essential data on Al, V, Se, La, Cs, and Sm. Although INAA was applied only to samples in the fine

fraction, coarse-particle INAA data for Na would have been helpful for improving the accuracy of the marine component. The wind-trajectory method identified five categories of stationary sources to include in the CMB. Perhaps more sources could have been identified if the sampling periods had been shorter than 12 h.

The composite method provided an estimate of the average Pb abundance in vehicle exhaust when incinerators and oil combustion contributed a portion of the Pb. Final CMB results indicate that the vehicle exhaust portion of PM-10 ranged from 4 to 6%. Stationary sources included in our CMB contributed less than 5% to PM-10. The sulfate component contributed 49–54% of PM-10 and consisted of sulfate plus related water and ions. Wind-stratified data indicated that 80 ± 20% of particulate S was from regional sources. Multiple linear regression of S vs tracers Se and either V or Ni attributed 72 ± 8 and 16 ± 5% of particulate S to coal- and oil-fired power plants, respectively.

Interpretations reported here are a few of the possibilities that we expect other investigators may attempt. Any investigator may obtain our data and source signatures on IBM-PC readable disks by sending a pair of 360-Kbyte diskettes or a single 1.2-Mbyte diskette to the corresponding author.

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Registry No. C, 7440-44-0; NH_4^+, 14798-03-9; Na, 7440-23-5; Al, 7429-90-5; Si, 7440-21-3; S, 7704-34-9; Cl, 7782-50-5; K, 7440-09-7; Ca, 7440-70-2; Sc, 7440-20-2; Ti, 7440-32-6; V, 7440-62-2; Cr, 7440-47-3; Mn, 7439-96-5; Fe, 7439-89-6; Co, 7440-48-4; Ni, 7440-02-0; Zn, 7440-66-6; Ga, 7440-55-3; As, 7440-38-2; Se, 7782-49-2; Br, 7726-95-6; Sr, 7440-24-6; Mo, 7439-98-7; Ag, 7440-22-4; Cd, 7440-43-9; In, 7440-74-6; Sn, 7440-31-5; Sb, 7440-36-0; I, 7553-56-2; Cs, 7440-46-2; La, 7439-91-0; Ce, 7440-45-1; Sm, 7440-19-9; W, 7440-33-7; Au, 7440-57-5; Pb, 7439-92-1.

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